Relative Ineffectiveness of Longicyclic Three-Ribbon Interactions in Dications. Rearrangement Products of Benzobarrelene Dications: An MNDO and Experimental Study†

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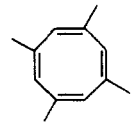
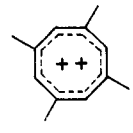
Abstract: NMR and quench experiments on superacid solutions of systems designed to yield benzobarrelene dication derivatives reveal only a cascade of rearrangement products. In accord with the results of MNDO calculations, possible longicyclic Möbius 4π-e aromaticity in derivatives of the barrelene dication is thus found to be ineffective. Coulombic repulsion appears to be a dominant factor in determining the structure of dication that will be favored. Diol precursors exhibit surprisingly specific modes of ionization, depending on their stereochemistry, and give different cationic intermediates. Diprotonated diketones rearrange selectively to give isomers with the bicyclo[3.2.1]octadiene framework, which may rearrange further to the more stable bicyclo[3.3.0]octadiene isomers. Two-electron oxidation of neutral benzobarrelenes also leads to a rearrangement cascade. Contrary to the concepts of bicyclo- and homoaromaticity, the bishomoantiaromatic bicyclo[3.3.0]octadienediyl-type dications are found to be the most stable isomers.

There is continuing interest in the synthesis of carbodications in nonnucleophilic, superacid media.[1-5] Because of strong Coulombic repulsion in such species, the only dications yet to be observed by NMR spectroscopy have the charged centers separated by at least two methylene groups and are stabilized either by conjugation or by substituents. Hence, doubly charged systems provide a sensitive test for stabilizing effects. For instance, the $(4n + 2)\pi$-aromatic systems[6-10] provided a further confirmation of Hückel's rule.[11,12] Thus, tetramethylcyclooctatetraene (**1**) undergoes a two-electron oxidation to yield the corresponding dication **2**.



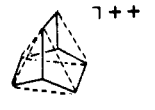
1, 8π electrons Hückel antiaromatic



2, 6π electrons Hückel aromatic

In contrast, the three-dimensional analogue of **1**, barrelene (**3**), is a 6π-electron Möbius antiaromatic system, as has been demonstrated via the heat of hydrogenation[13] and by photoelectron spectroscopy.[14] Goldstein[15,16] first treated this destabilization using qualitative MO theory. In analogy to cyclooctatetraene, a two-electron oxidation of **3** should yield the Möbius aromatic system **4**.

3, 6π electrons Möbius antiaromatic



4, 4π electrons Möbius aromatic

However, MINDO/3 calculations on C_8H_8 dications[17] revealed no minimum for a structure like **4** with the bicyclo[2.2.2] framework. We now report the results of a variety of possible synthetic approaches to derivatives of the barrelene dication **4**. These experimental studies have been combined with semiempirical MO calculations on benzobarrelene dications and their isomers.

Semiempirical Calculations

In order to clarify the contradictions between simple qualitative MO predictions and the MINDO/3 results,[17] we first performed MNDO[18] calculations in order to assess the probability of observing **4** or its rearrangement products. We chose MNDO for these calculations because of some inconsistencies between MINDO/3 results and experimental observations. For instance,

† Dedicated to G. A. Olah on his 60th birthday.

(1) (a) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985; Chapter 3.4.11. (b) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem.* **1983**, *95*, 356. (c) Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1986**, *108*, 836. (d) Olah, G. A.; Prakash, G. K. S.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764. (e) Prakash, G. K. S.; Krishnamurthy, V. V.; Arnanaghi, M.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 3985. (f) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Org. Chem.* **1982**, *47*, 3903. (g) Olah, G. A.; Grant, J. L.; Spear, R. J.; Bollinger, J. M.; Serianz, A.; Sipos, G. *J. Am. Chem. Soc.* **1976**, *98*, 2501. (h) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Am. Chem. Soc.* **1980**, *102*, 6127. (i) Bollinger, J. M.; Cupas, C. A.; Friday, K. J.; Woolfe, M. L.; Olah, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 156. (j) Olah, G. A.; Liang, G.; Paquette, L. A.; Melega, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 4327.

(2) (a) De Meijere, A.; Schallner, O.; Mateescu, G. D.; Gölitz, P.; Bischof, P. *Helv. Chim. Acta* **1985**, *68*, 1114. (b) De Meijere, A.; Schallner, O.; Gölitz, P.; Weber, W.; Schleyer, P. v. R.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 5255.

(3) Pagni, R. M. *Tetrahedron* **1984**, *40*, 4161.

(4) (a) Willner, I.; Rabinovitz, M. *J. Am. Chem. Soc.* **1978**, *100*, 337. (b) Willner, I.; Becker, J. Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1979**, *101*, 395. (c) Trost, B.; Bright, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4244. (d) Trost, B.; Kinson, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 2438. (e) Hogeveen, H.; Kruchten, E. M. G. A. v. *J. Org. Chem.* **1981**, *46*, 1350. (f) Giordano, C.; Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* **1977**, *99*, 5181. (g) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413. (h) Hogeveen, H.; Kwant, P. W. *J. Am. Chem. Soc.* **1974**, *96*, 2208. (i) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257. (j) Bremer, M.; Schleyer, P. v. R.; Schötz, K.; Kausch, M.; Schindler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 761; *Angew. Chem.* **1987**, *99*, 795.

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(6) Olah, G. A.; Staral, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 6290.

(7) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 6045.

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(10) Olah, G. A.; Staral, J. S.; Paquette, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 1267.

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(12) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3345.

(13) (a) Turner, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 3586. (b) Yamamoto, S.; Nakata, M.; Fukuyama, T.; Kuchitsu, K.; Hasselmann, D.; Ermer, O. *J. Phys. Chem.* **1982**, *86*, 529.

(14) Haselbach, E.; Heilbronner, E.; Schröder, G. *Helv. Chim. Acta* **1971**, *54*, 153.

(15) Goldstein, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 6357.

(16) Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193.

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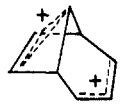
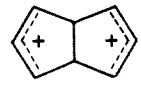
the bicyclic dication **5**, which is experimentally unknown, was calculated[17] to be slightly more stable than its isomer **6**, but both were found to be more than 20 kcal mol^{-1} less stable than the cyclooctatetraene dication. Experimentally, however, derivatives of the cyclooctatetraene dication undergo a ring-closure reaction to give derivatives of the bicyclo[3.3.0] dication **6**.[10]



5



6

In contrast to MINDO/3, MNDO predicts the cyclooctatetraene dication and **6** to have comparable stabilities.[19] The known tendency[18,20] of MNDO to prefer classical structures, in contrast to MINDO/3,[21] may lead to an unrealistic relative destabilization of nonclassical structures. However, MNDO performs better than MINDO/3 for polycyclic structures;[18,22] this makes it more suitable for our purposes. We are now comparing the results of a variety of semiempirical calculations with these obtained by ab initio methods.

In order to relate the calculational results more closely to the experimental systems, we performed calculations on the benzobarrelene dication and its isomers. In view of the predicted instability of the barrelene dication itself, and because of the relatively easy accessibility of substituted benzobarrelenes, these stabilized systems appeared best suited for both experimental and theoretical studies.

The MNDO results for the benzo-C_8H_6 dications **7–18** are shown in Chart I. In accord with experimental expectations, the bicyclo[3.3.0] dication derivative **18** is calculated to be the most stable structure of those investigated. The cyclooctatetraene ring-closure reaction (**17** to **18**) is indicated to be exothermic by 17.3 kcal mol^{-1}. The bicyclo[3.2.1] dication derivatives **14–16** are found to be 20–30 kcal mol^{-1} less stable than the benzocyclooctatetraene dication **17**. The dications **10–13**, which are all interconvertible and can give dications **14–16** via cyclopropylcarbinyl–cyclobutyl–homoallyl rearrangements, are calculated to have heats of formation in the 566–585 kcal mol^{-1} range, i.e., more than 50 kcal mol^{-1} less stable than **18**. The three possible "barrelene" dications **7–9** are even less stable; their heats of formation range between 590 and 605 kcal mol^{-1}. All structures were shown to be minima by diagonalization of the Hessian matrix, except **8**, **11**, and **15**, which are transition states for the degenerate rearrangements of **10**, **13**, and **16**, respectively.

These results strongly suggest that attempts to generate dications based on the benzobarrelene framework should result in a cascade of rearrangements that would lead eventually to derivatives of the bicyclo[3.3.0] dication **18**. Under suitable conditions, derivatives of **14–17** may be observable, depending on the kinetics of the rearrangement to **18**. The C_1 structure **16** is, however, possibly an artifact of MNDO's preference for classical structures, so that the C_s dication **15** may be the true minimum energy structure in this region of the potential energy surface.

Results

As discussed above, it was decided to provide extra stabilization for possible dications with a bicyclo[2.2.2]octadiene framework by inclusion of a benzo-annulated ring in the neutral precursor. The ketones **19** and **20** represent ideal starting materials, because not only can they be doubly protonated under stable ion conditions but they also can be converted to the diols **21** and **22** by methyllithium additions to the carbonyl groups. Both **21** and **22** are

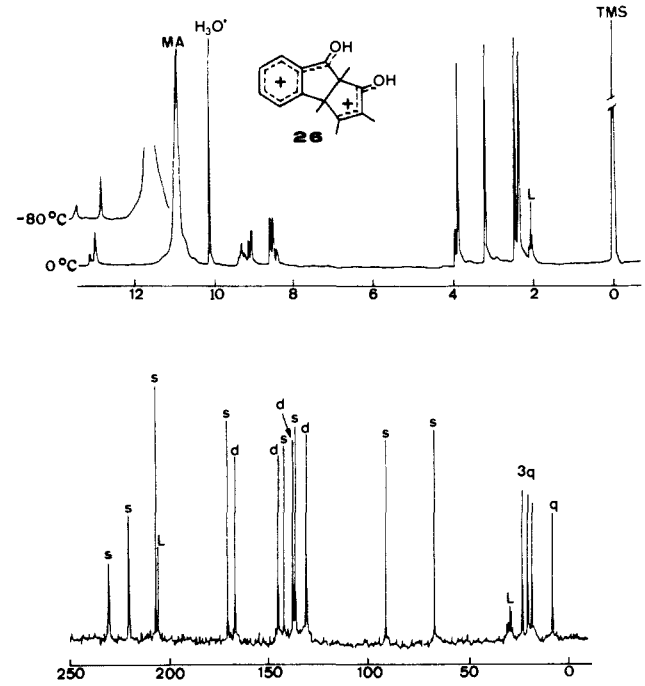
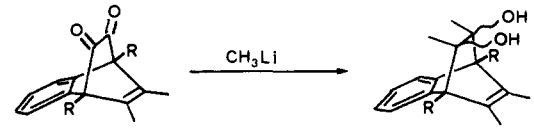


Figure 1. ^1H (100-MHz) and ^{13}C (25-MHz) NMR spectra of the doubly protonated dione **26**; (L, acetone-d_6).

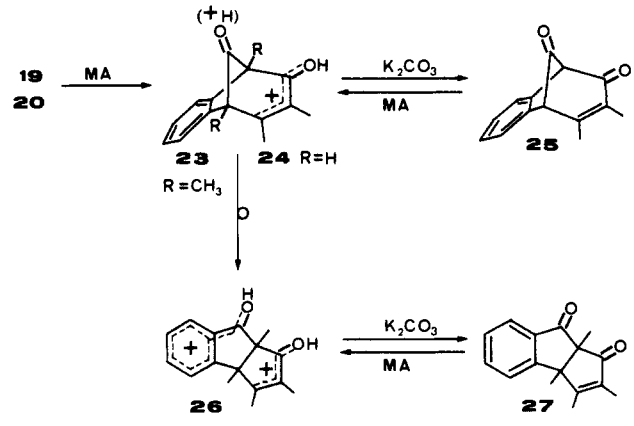
promising highly methylated precursors for barrelene dication systems ("anti" and "syn" are relative to the isolated double bond).



19: R = Me
20: R = H

21t: R = Me, OH trans
21a: R = Me, OH cis, anti
21s: R = Me, OH cis, syn
22t: R = H, OH trans
22a: R = H, OH cis, anti
22s: R = H, OH cis, syn

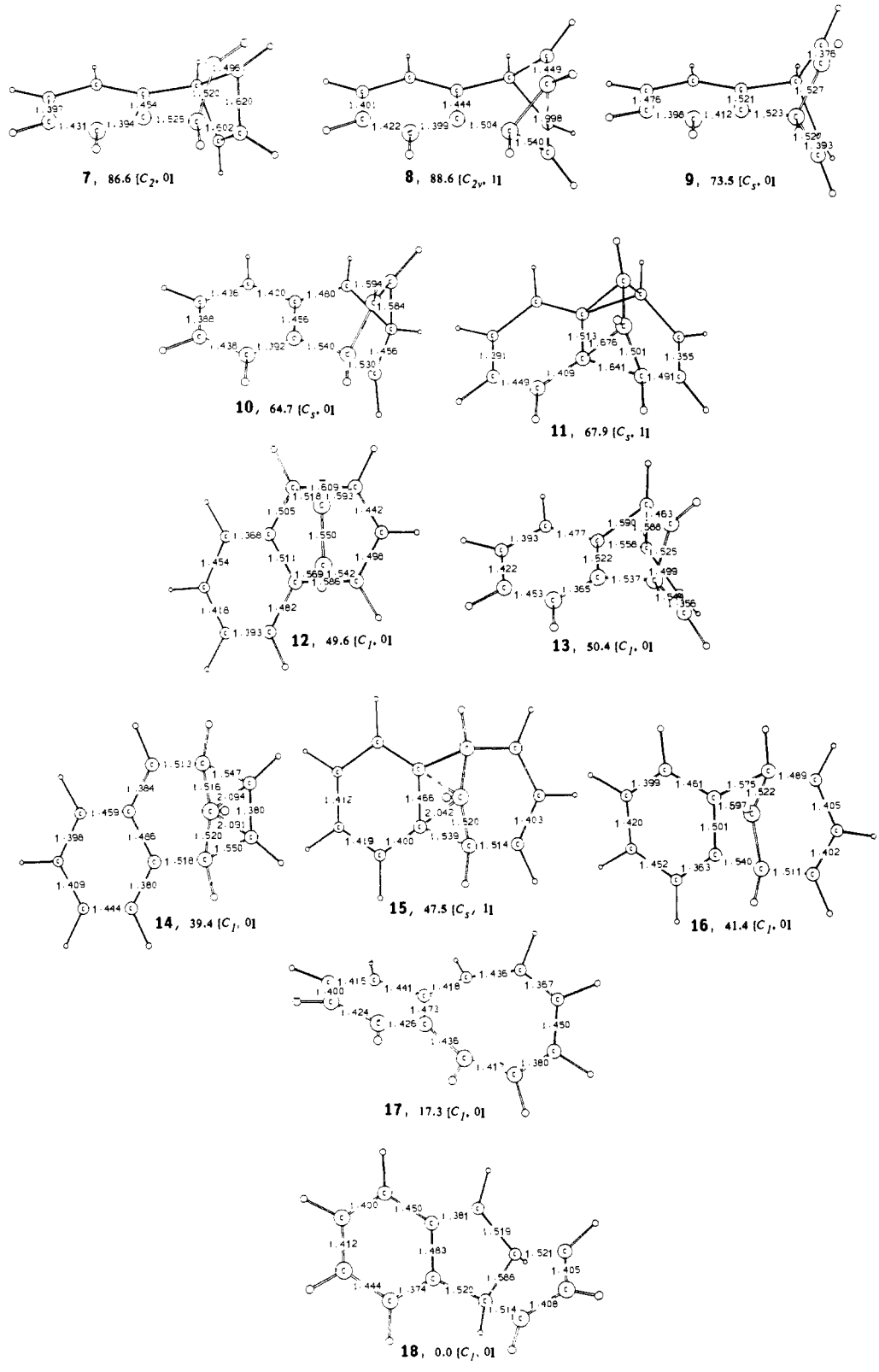
Double Protonation of Diones 19 and 20. Reaction of **19** and **20** with at least a fivefold molar excess of SbF_5/FSO_3H (1:1; magic acid, MA) in SO_2ClF at −90 °C resulted in solutions that gave the NMR data summarized in Chart II. These spectra and the results of quenching experiments with K_2CO_3 are compatible with the following reaction scheme:



The individual structural features can be deduced by comparison with the known cations **28–30**[23,24] (Chart II). The structure of

(18) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.
(19) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Davies, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, *558*.
(20) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231; *Inorg. Chem.* **1978**, *17*, 1569.
(21) (a) Köhler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479. (b) Wenke, G.; Lenoir, D. *Tetrahedron* **1979**, *35*, 489.
(22) McManius, S. P.; Smith, R. M., Smith, M. B.; Schafer, S. G. *J. Comput. Chem.* **1980**, *1*, 233.
(23) Olah, G. A.; Halpern, Y.; Mo, Y. K.; Liang, G. *J. Am. Chem. Soc.* **1972**, *94*, 3554.

Chart I: Calculated Structures of the Benzo-C_8H_6 Dications **7–18** with Relative Energies (kcal mol^{-1}) (Symmetry Conditions, Imaginary Frequencies, and Bond Lengths (Å) Given)



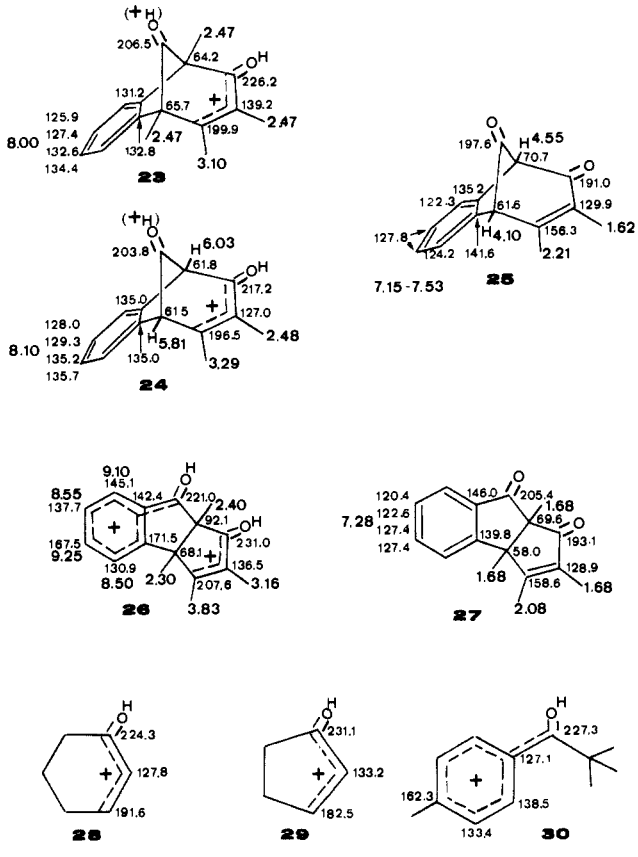
the quench product **25** was confirmed by the INADEQUATE two-dimensional NMR technique.[25] The 1,3-diketone arrangement in **27** was demonstrated by using Eu(fod)$_3$ shift reagent.[26] Neither in the bicyclo[3.2.1] systems **23** and **24** nor in **26** can the double protonation be seen from integration of the ^{1}H NMR spectra (shown in Figure 1). The double positive charge in **26** follows from the ^{13}C chemical shifts (^{13}C total chemical shift difference[27] δ(**26**)–δ(**27**) = 299.6 ppm), but this is not possible

(24) Barthelemy, J.-F.; Jost, R.; Sommer, J. *Org. Magn. Reson.* **1978**, *11*, 443.

(25) (a) Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2102. (b) Mareci, T. H.; Freeman, R. *J. Magn. Reson.* **1982**, *48*, 158.

(26) (a) Wilt, J. W.; Niinemae, R. *J. Org. Chem.* **1980**, *45*, 5402. (b) Crumine, D. S.; Yen, H.-H. B. *J. Org. Chem.* **1976**, *41*, 1273.

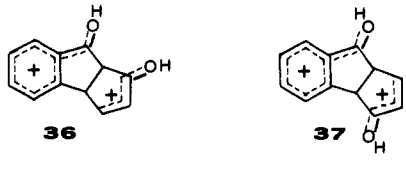
Chart II: Selected ^1H (Large Numbers) and ^{13}C (Small Numbers) NMR Chemical Shift Data of the Cations **23**, **24**, and **26** Compared with Those of the Neutral Compounds **25** and **27** and the Reference Systems **28–30**



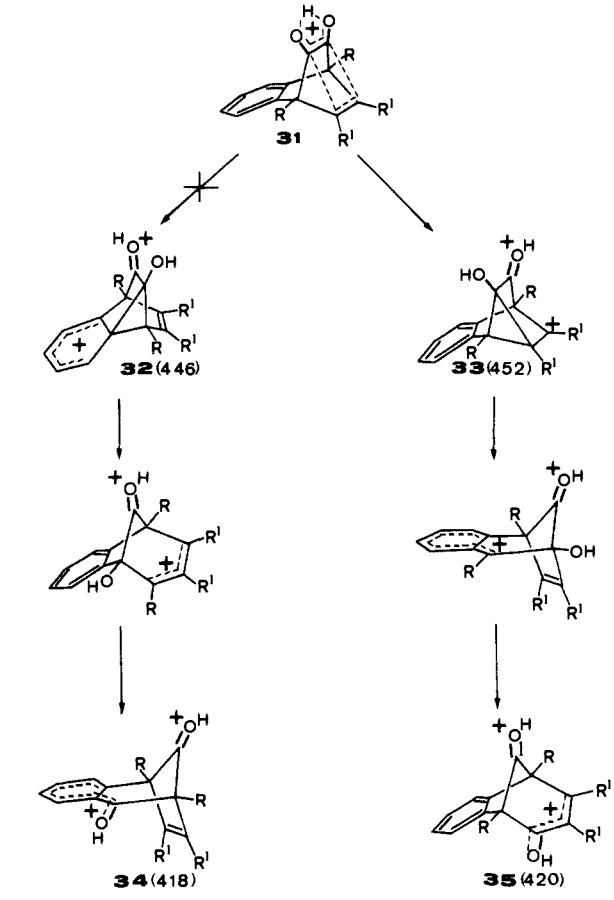
for **23** and **24**. Therefore, the exact nature of **23** and **24** cannot be determined, although a doubly protonated species is likely by analogy with **26**.

In accord with the predicted instability of dications with barrelene-like framework, no doubly protonated species of this form could be observed below −90 °C. MNDO provides no thermodynamic rationalization for the specific rearrangement of **19** and **20** to **23** and **24**, respectively, in the doubly protonated systems. Scheme I shows the MNDO-calculated heats of formation of models for the rearrangement of doubly protonated **20** and **24**. The two alternative pathways leading to either **34** or to **35** via **32** and **33**, respectively, should be very similar energetically in the dimethyl and tetramethyl systems because of the extra stabilization of **33** by the methyl group, R's on the carbocationic center. Experimentally, however, only one of these alternatives, that leading to **24** (for which **35** is a model), is observed. However, it is possible that the rearrangement takes place at the monoprotonated stage and that the observed dications are obtained by the protonation of a monocation rearrangement product.

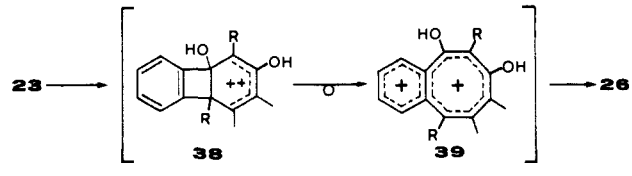
Similarly, MNDO indicates no thermodynamic preference for the product of the subsequent substituent-dependent rearrangement to the bicyclo[3.3.0] dication **26**. Of the isomeric model diprotonated diketones, **37**, which does not correspond to the product found in the experimental system, is predicted to be 2.4 kcal mol^{-1} more stable than **36**, which corresponds in structure to **26**.



Scheme I: Rationalization of the Rearrangement of the Benzobarrelenediones **19** and **20** to the Bicyclo[3.2.1]octadiene Isomers **23** and **24** (MNDO Energies (kcal mol^{-1}) of the Model Compounds **32–35** (R = R′ = H) Are Given)



The mechanism can be formulated as a specific 1,2-shift in **23** to give **38**, which then ring opens to the benzocyclooctatetraene derivative **39**, which in turn undergoes the known ring closure to yield **26**.

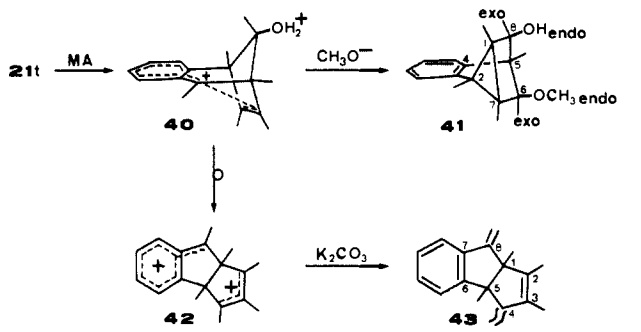


The reluctance of the dimethyl species **24** to rearrange can be rationalized if the energetically unfavorable intermediate **38** is close to the energy maximum. Rearrangement is facilitated by the two extra methyl groups in **23**, which provide extra stabilization in **38** (R = CH_3 instead of H) and also facilitate ring opening to **39**.

Ionization of Diols 21 and 22. In contrast to the simple double protonation of diketones discussed above, ionization of the diols **21** and **22** involves protonation and subsequent dehydration. This difference in mechanism may favor polycyclic structures because the carbocationic center is not produced directly in the protonation step. The precooled solid diols were added slowly with vigorous mixing to at least a fivefold excess of MA (SbF_5/FSO_3H, 1:1, magic acid) in SO_2ClF at −110 to −130 °C. The ^1H and ^{13}C NMR data of the ions (shown in Chart III) and of the quench products (see the Experimental Section) indicated that both the stereochemistry of the OH groups and the nature of the bridgehead substituents influence the behavior on ionization. Thus, *trans*-diol **21t** ionizes to yield cation **40** with a benzylic moiety. Comparison with data for the indenyl cation **44**[28] suggests that **40** benefits from

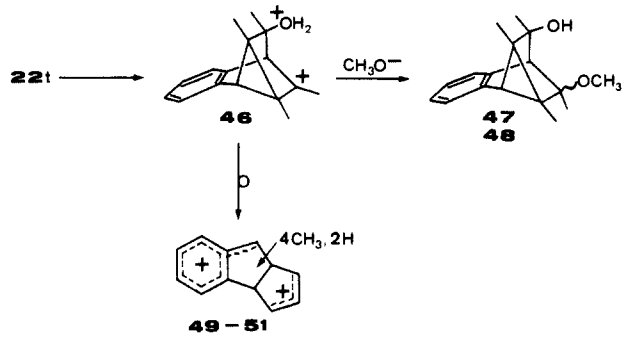
(27) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(28) Olah, G. A.; Asensio, G.; Mayr, H. *J. Org. Chem.* **1978**, *43*, 1518.



a homoallylic stabilization. Quenching with methoxide appears to confirm this interpretation, since the tetracyclic species **41** is formed. Dication **40** is not stable above −30 °C but rearranges with loss of a second water molecule to form the bicyclo[3.3.0]-octadienyl dication **42** (Figure 2). The presence of the allyl moiety in **42** can be deduced from a comparison with the reference system **45**. Quenching with K_2CO_3/ice gives the benzotriene **43**.

The homologous tetramethyl derivative **22t**, in contrast, forms a largely localized cation **46** below −50 °C. The cyclopropyl-carbinyl moiety in **46** gives similar NMR data to that in the dehydroadamantyl cation **52**.[29] The stereochemistry of **46** was determined by quenching with methoxide to give the isomeric derivatives **47** and **48**. Above −50 °C, **46** rearranges unspecifically to three isomers **49–51** with a bicyclo[3.3.0] framework. Only **51** could be observed in this mixture after 7 days at −30 °C.



The substituent pattern on the allylic moiety is deduced from comparison with data for the bicyclic dication **45** and the trimethylallyl cation **53**.[30] The protons positions can be determined from the chemical shifts of the bridgehead carbons. These chemical shifts depend on the sum of the chemical shifts of the neighboring positive centers. Figure 3 shows the nearly linear correlation obtained by plotting the sum of the chemical shifts of the α-carbons against the chemical shifts of the bridgehead atoms. In general, it can be concluded from Figure 3 that bridgehead carbon atoms with δ values above 79 ppm are β to the aromatic ring, whereas those below 79 ppm occupy a position α to the ring. The structures of **49–51** are established by use of these criteria. Quench reactions with K_2CO_3 and with methoxide ion gave no further confirmation, but only complex product mixtures.

The *anti*-diols **21a** and **22a** showed a much more complex behavior on ionization, which depended strongly on differences in experimental conditions. The hexamethyl derivative **21a** gave a mixture of the bicyclo[3.3.0]octadiene derivative dication **42** and the protonated allyl cation **54** (compare reference compound **57** in Chart III); the ratio varied with the mixing temperature (−100 to −120 °C; NMR measurements all at −80 °C). The stereochemistry of **54** was determined by quench reactions with methoxide, which gave derivative **55**. If, however, the reaction mixture was kept below −130 °C during mixing and subsequently measured at −105 °C, neither **42** nor **54** could be observed, but

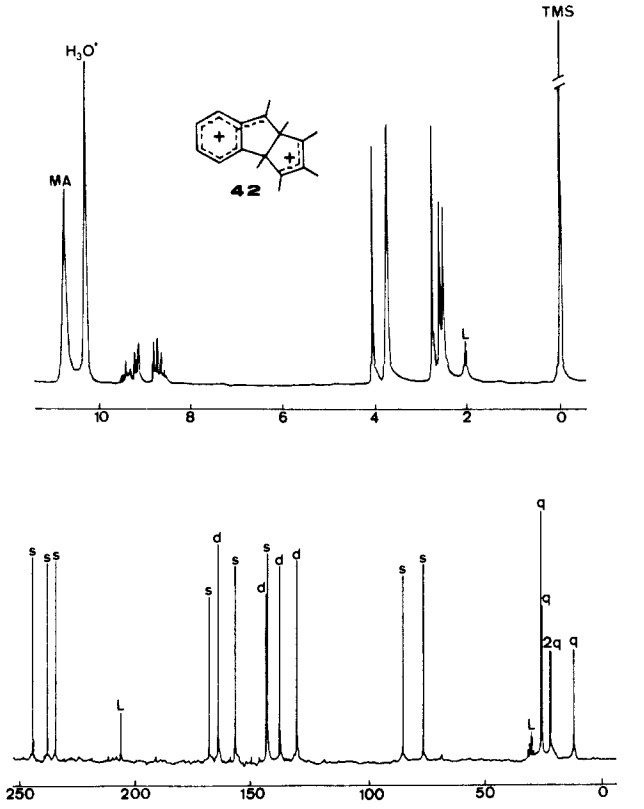


Figure 2. ^1H (100-MHz) and ^{13}C (25-MHz) NMR spectra of the dication **42**; (L, acetone-d_6).

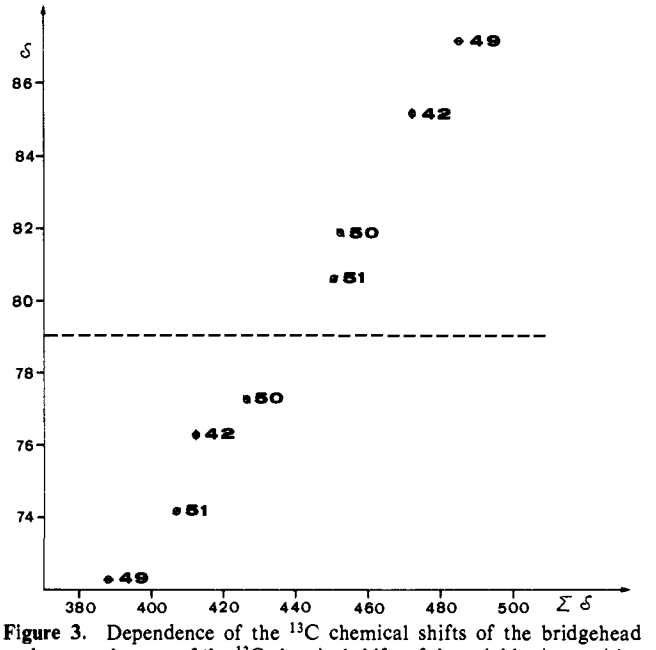
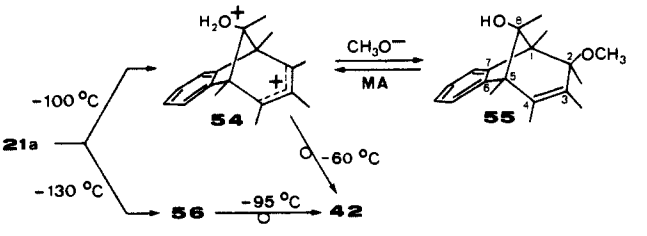


Figure 3. Dependence of the ^{13}C chemical shifts of the bridgehead carbons on the sum of the ^{13}C chemical shifts of the neighboring positive centers (for data see Chart III).

rather an unidentified ion **56**,[31] which rearranged to **42** above −95 °C. Similarly, **54** gives **42** on warming to −60 °C.



(29) Olah, G. A.; Liang, G.; Babiak, K. A.; Ford, T. M.; Goff, D. L.; Morgan, T. H., Jr.; Murray, R. K., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 1494.
(30) Olah, G. A.; Mayr, H. *J. Am. Chem. Soc.* **1976**, *98*, 7333; **1978**, *100*, 6544.

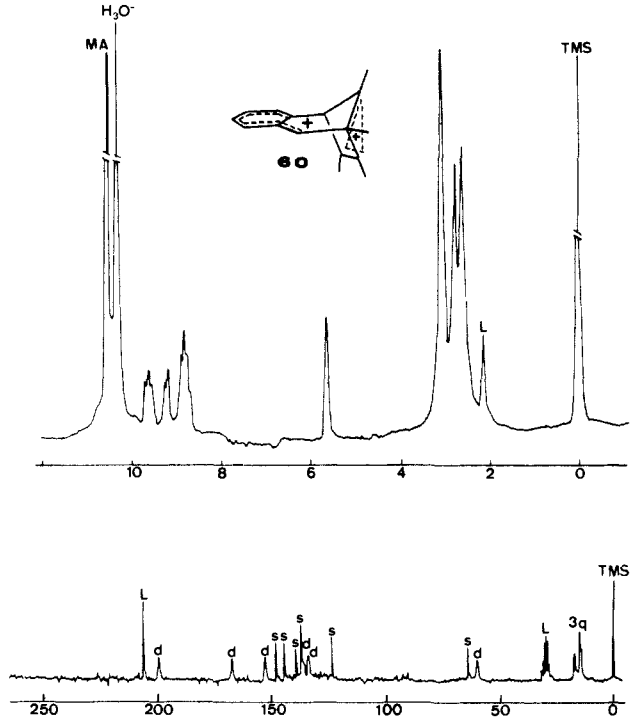
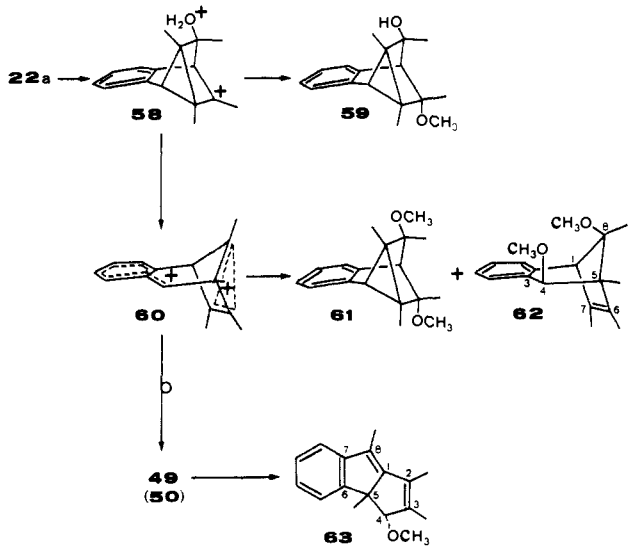


Figure 4. ^1H (100-MHz) and ^{13}C (25-MHz) NMR spectra of the bicyclo[3.2.1] dication **60**; (L, acetone-d_6).

In contrast to **21a**, **22a** ionizes (analogously to **22t**) to form **58** with a cyclopropylcarbinyl moiety; the methoxide quench product **59** is a yet another isomer of **47** and of **48**. When the temperature



is raised, the ^{13}C NMR spectrum of dication **60** can be observed (Figure 4) and is persistent for up to 2 h (an oil forms in the reaction mixture). The dicationic nature of **60** is shown by the methoxide quench products **61** and **62**. The structure of **62** was confirmed by difference NOE experiments.[32] However, **60** is not stable above −70 °C but rearranges under mild conditions (slow warming) selectively to the bicyclo[3.3.0] isomer **49**. However, if the mixture is agitated vigorously and warmed in order to try to keep the resulting oil in solution, a mixture of **49** and **50** is obtained. Methoxide workup of **49** is consistent with an elimination product **63**, whose configuration is determined by the dication structure.

In contrast to the compounds discussed above, **21s** does not react by loss of a OH_2 group but rather via protonation of the double

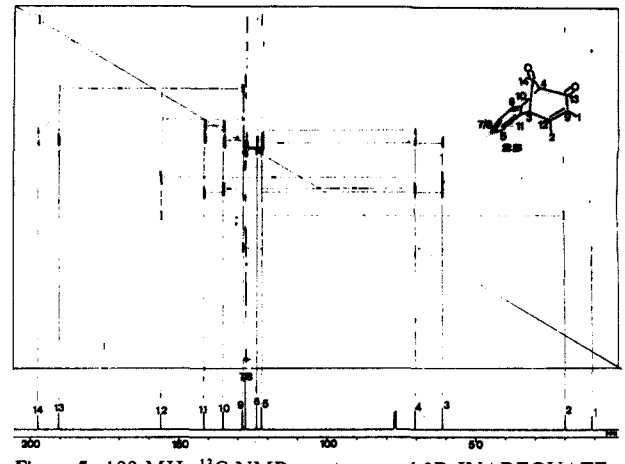


Figure 5. 100-MHz ^{13}C NMR spectrum and 2D-INADEQUATE contour plot of diketone **25**. The standard 2D-INADEQUATE sequence with 32-step phase cycling was used. The data on the JEOL JNM-GX-400 were as follows: CLPNT = 64 with zero filling to 128, SCANS = 128; FREQU = 16835.0 Hz; OBFRQ = 100.5 Hz; PD = 6.30 μs; POINT = 8192; PW1 = 15.5 μs; experimental line broadening in t_2; Lorentzian to Gaussian transformation in t_1. The compound was dissolved in $CDCl_3$ with 2 mol % chromium acetylacetonate. The numbers on the signals in the ^{13}C NMR spectrum are related to those in the formula.

	1	2	3	4	5	6	7	8	9	10	11	12
1		o	o				o	o				
2	o				o	o						
3	o			+				●				
4			+		●							
5		o		o		+			●			
6		o			+				o			
7	o							●				o
8	o		o				●					o
9					●	o				o		
10									o		o	
11										o		o
12							o	o			o	

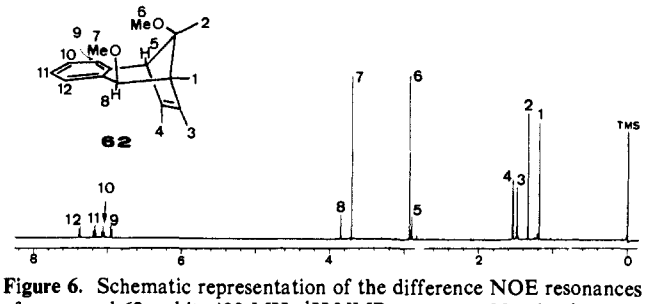


Figure 6. Schematic representation of the difference NOE resonances of compound **62** and its 400-MHz ^1H NMR spectrum. Number in a row is the irradiated signal of the ^1H NMR spectrum; number in a column is the resonance of signal. Relative intensities: o, weak; O, strong, ●, very strong. The symbol + means that this signal is also irradiated when the neighboring peak is irradiated.

bond. A mixture of two isomeric dications **64** and **65** is obtained, depending on the reaction conditions (**64**:**65** = 4:1 at −100 °C, 1:1 at −80 °C). The carbocationic entities of **64** and **65** are related to the homobenzylic moiety in the bicyclic derivative **68**,[33] which has similar spectroscopic characteristics. However, no methyl ethers were obtained on methoxide workup, but rather the cyclic

(31) Principal signals in the ^{13}C NMR spectrum are at 214.7, 198.6, 148.0, 131.9, 120.9, 109.7, 80.2, 74.0, 59.5, and 53.9 ppm.

(32) Feeney, J.; Partington, P. *J. Chem. Soc., Chem. Commun.* **1973**, 611.

(33) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1976**, *98*, 6304.

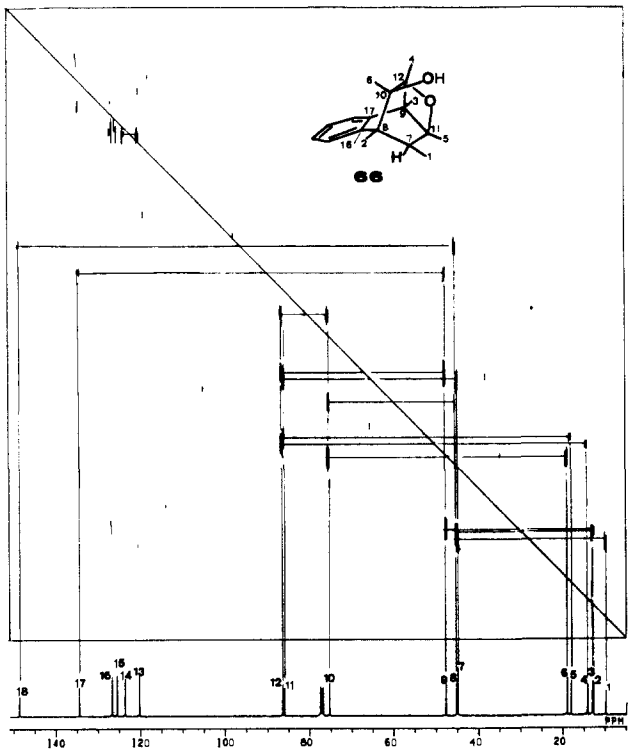
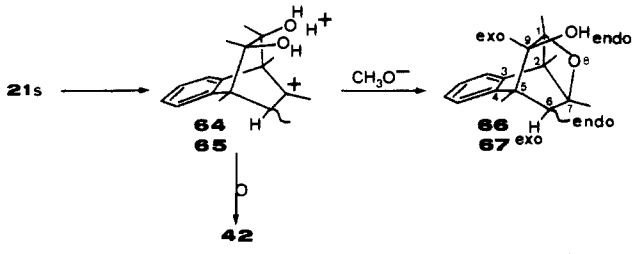


Figure 7. Contour plot of the 2D-INADEQUATE measurement of **66** and its 100-MHz ^{13}C NMR spectrum. Measurement conditions: FREQU = 20491.8 Hz; PW1 = 15.4 μs. Otherwise, see Figure 5.

ethers **66** and **67**. Their structures were assigned by 2D-INADEQUATE and difference NOE experiments (see the Experimental Section). Cations **64** and **65** are relatively stable and only rearrange fully to **42** after about 30 min at 5 °C.

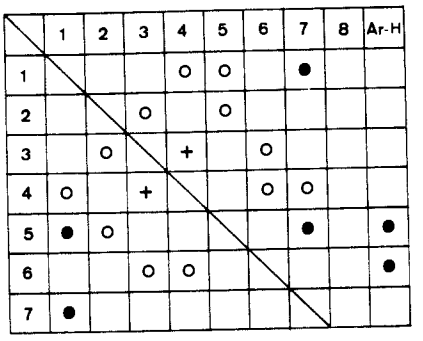


The behavior of **22s** is complex and could not be elucidated. With MA at −100 °C no signal above 140 ppm in the ^{13}C NMR spectrum is observed. At −80 °C unselective rearrangement to several unknown products occurs. No simplification was obtained if this spectrum was observed at higher temperatures, and above −25 °C polymer evidently formed.

Discussion

Cation Formation. The isomeric and homologous compounds **21** and **22** lead to carbocations, which are surprising in their variety and formation selectivity. Three effects are responsible. In the first ionization step, the magnitude of the backside participation is of decisive importance. Only those protonated alcohols that are activated by the isolated double bond (**21t,a**, **22t,a**) are ionized (shown in A), whereas the alternative phenonium interaction[33,34] in the corresponding epimers (**21s**) is not sufficient to promote ionization. Instead, proton addition then becomes competitive (B). The relatively poor effectiveness of the aromatic participation also leads to byproducts in ethylene arenium systems.[35]

(34) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 2236.



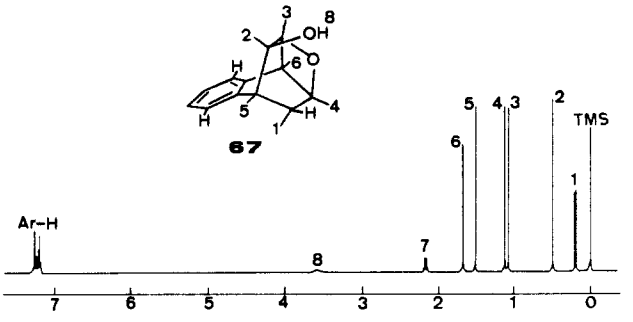
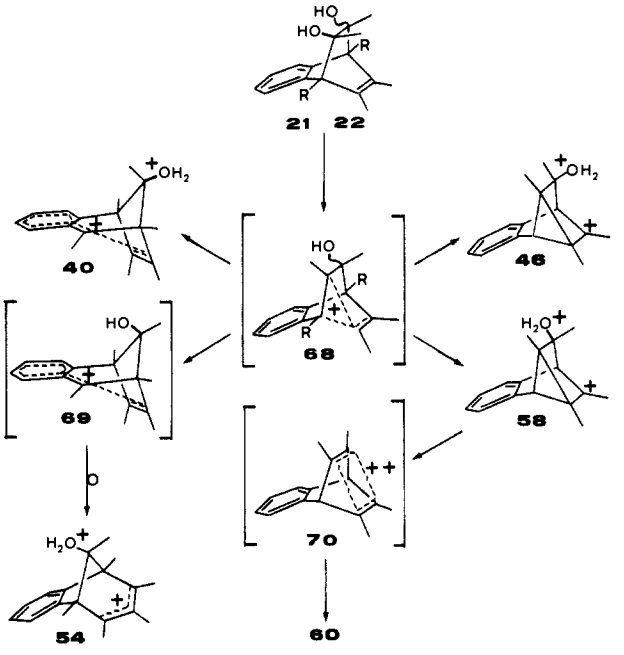


Figure 8. Schematic representation of the difference NOE resonances of compound **67**. Key to symbols as with Figure 6.

Scheme II: Overview of the Ionization Behavior of the Benzobarrelenediols **21** and **22**

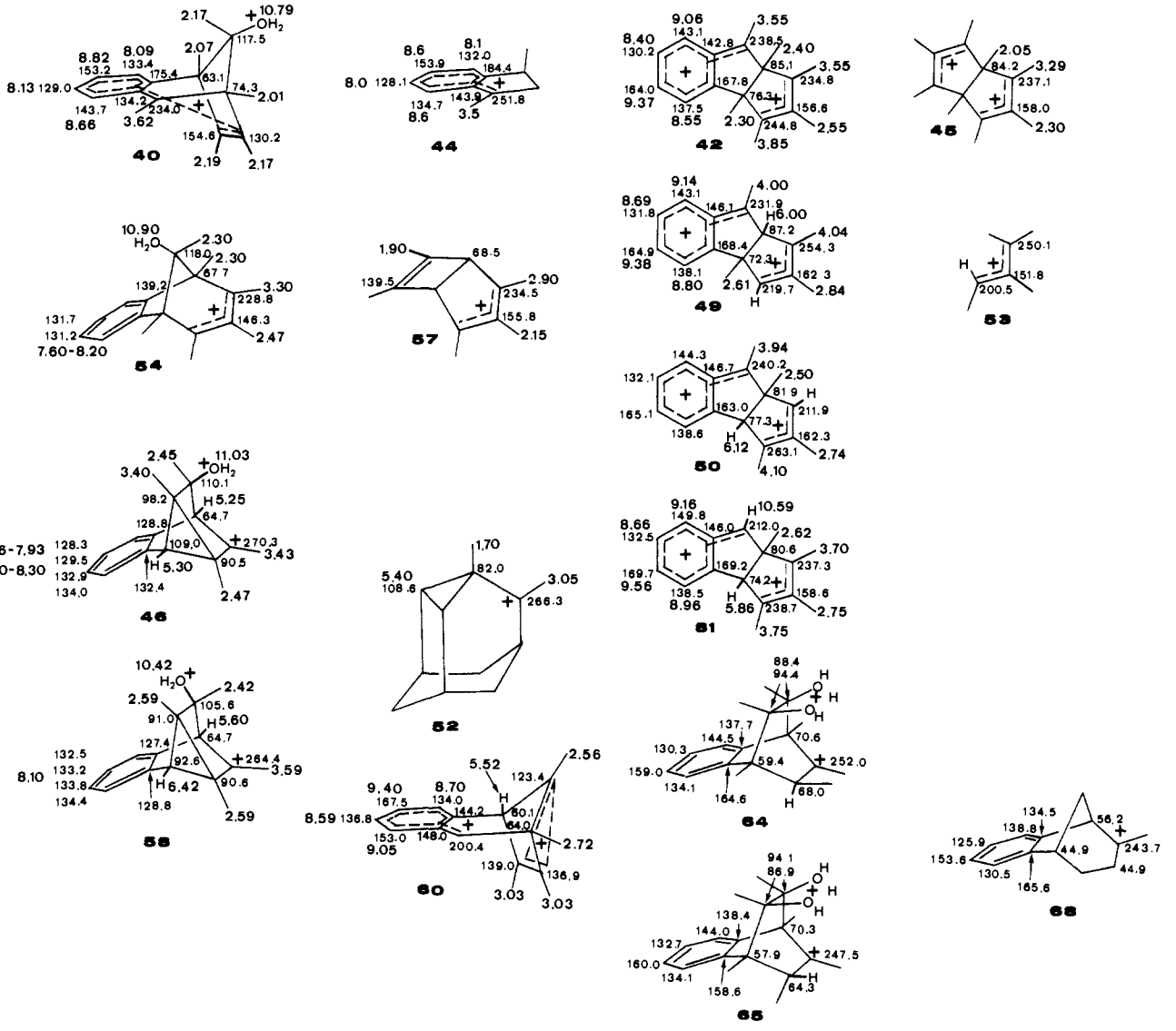


In the next step, the best placement of the positive charge in the bicyclic skeleton becomes dominant. Stabilization can be achieved in tertiary cyclopropylcarbinyl or tertiary or secondary benzylic cation entities. In the tetramethylbenzobarrelenes, the cyclopropylcarbinyl cations **46** and **58** are preferred (Scheme II). In contrast, the hexamethyl derivative **21t** forms **40**, which is primarily a tertiary benzylic cation.

The final rearrangement, only observed for **21a**, leads to the protonated bicyclo[3.2.1]octadienyl cation alcohol[36] **54**. At ca.

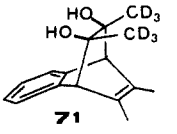
(35) (a) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6877. (b) Olah, G. A.; Pittmann, C. U., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3509, 3507. (c) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 7627. (d) Olah, G. A.; Comisarow, M. B.; Kim, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 1458.

Chart III: Selected ^1H (Large Numbers) and ^{13}C (Small Numbers) Chemical Shift Data of the Cations Formed by Ionization of the Benzobarrelenediols **21** and **22**. Reference Systems Are Given on the Right-Hand Side (^1H NMR Chemical Shifts Refer to Internal TMS in Capillary, ^{13}C NMR Chemical Shifts Refer to Internal TMS in Acetone Capillary)

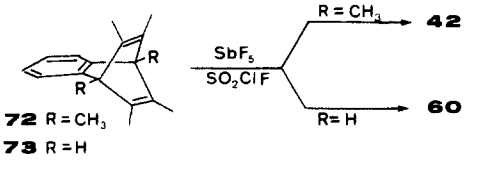


−110 °C a fast 1,2-shift from intermediate **69** can occur before the second protonation gives **54** (see Scheme II). At even lower temperatures, this Wagner–Meerwein shift is apparently slowed down enough that the protonation of the second OH group leads to the unidentified cation **56**.

Dication Formation. Loss of water from the protonated hydroxy cations (**40**, **46**, **54**, **58**) to give hydrocarbon dications is only expected when such ionizations occur at a lower temperature than rearrangement. The rate of the H_2O loss is dependent both on the stability of the product dication and on the stereochemistry of the leaving groups. The configurations in **40** and **54** are unfavorable; assisted ionization is not expected to be effective, although the participation of a bishomocyclobutadienyl unit[37] is conceivable. The situation is equally unfavorable in **46** and **58**. In **46** only a weak phenonium type interaction is possible, whereas in **58** the only neighboring group participation involves the three-membered ring, which is already engaged in stabilizing. Nevertheless, this configuration leads to dications at sufficiently low temperatures. A bishomocyclobutadienyl dication-like transition state or intermediate such as **70** may favor this process. The deuteriated compound **71** gives a statistical distribution of the deuteriomethyl groups in dication **60**. Hence, a symmetrical intermediate is required. In the stereoisomer **46**, such neighboring group participation is not possible and a higher barrier for the second ionization results.

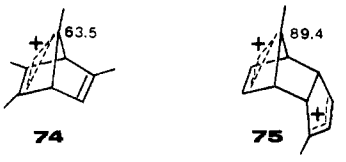


Attempts to observe bicyclo[2.2.2]octadienyl dications by generation at even lower temperatures always resulted in rearranged products, even by direct 2e oxidation of barrelenes **72** and **73** at −130 °C with SbF_5. As the corresponding radical cations are persistent,[38] the rearrangement must take place during or after the second ionization.



(36) Hart, H.; Jiang, J. B.-C.; Sasaoka, M. *J. Org. Chem.* **1970**, *42*, 3840.
(37) Carnadi, H.; Giordano, C.; Heldeweg, R. F.; Hogeveen, H.; Kruchten, E. M. G. A. v. *Isr. J. Chem.* **1981**, *21*, 229.
(38) Clark, T.; Courtneidge, J. L.; Davies, A. G.; Schötz, K. *J. Chem. Soc., Chem. Commun.* **1986**, 547.
(39) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem.* **1983**, *95*, 356.

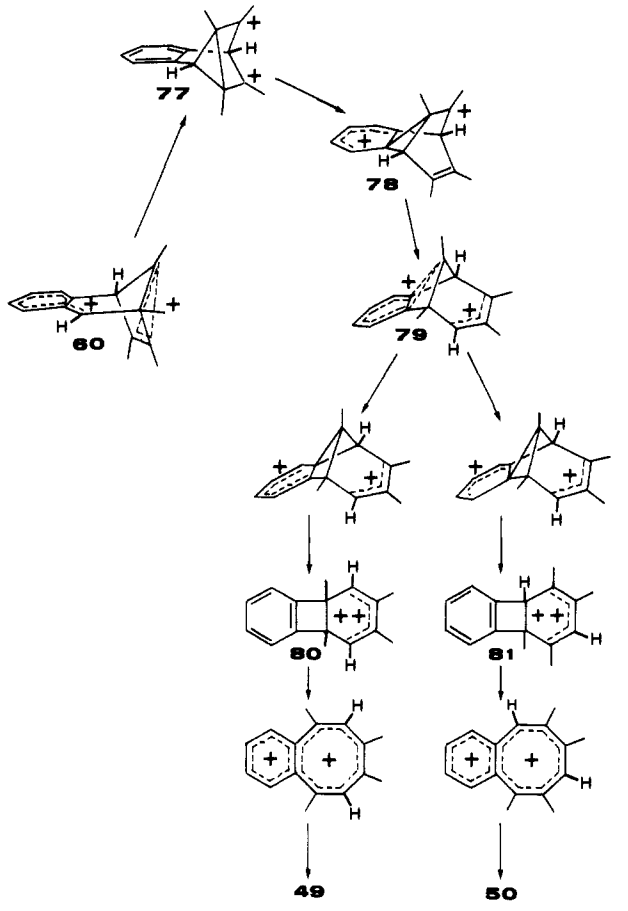
Bicyclic Interaction. Although no bicyclo[2.2.2]octadiene dications were detected, the involvement of a three-dimensional π interaction (i.e., $4n$ Möbius aromaticity) might be shown by the spectroscopic data for the ion **60**. This species involves 4π electrons in the [3.2.1] skeleton and belongs, as the barrelene dication does, to Goldstein's longicyclic category.[15,16] Comparison with the reference ions **44**, **74**,[40] and **75**[41] clearly shows an interaction between the two positively charged systems. There is

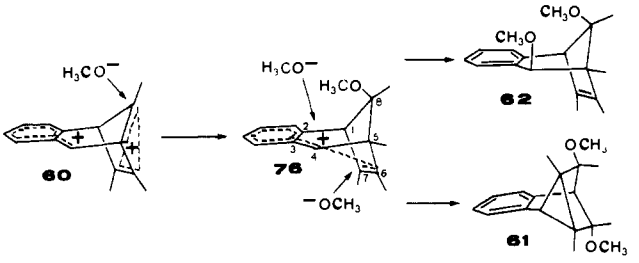


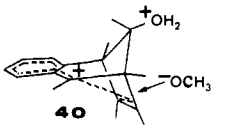
more positive charge on the hydrogen in these dications than in the comparable monocations (a general low-field ^{1}H NMR shift), and hence a balancing high-field shift can be expected for the ^{13}C NMR resonances.[39] Our system (**60**) is analogous; the positive charge is delocalized to the extremities of the aromatic system. The bishomocyclopropenium unit behaves similarly, although modified by a rehybridization effect. The chemical shift of C_8 (123.4 ppm) continues the series starting with **74** and **75**: the increase in p character at the one-carbon bridge is due to the repulsion between the positive charges. This is larger in **60** than in **75** and, of course, is not present at all in the monocation **74**. It is particularly interesting to compare the pericyclic *antiaromatic* dication **51** with the longicyclic *aromatic* species **60**. The benzyl units have very similar ^{13}C shifts except for one ipso and the benzylic carbon, which are shifted 12 and 15 ppm, respectively, to higher field in **60**. We believe that this small difference does not warrent classifying **60** as aromatic and suggest that the longicyclic interaction in this three-ribbon system is not very effective. Note, however, that this conclusion may not be valid for four-ribbon systems such as that recently studied by Olah et al.[52]

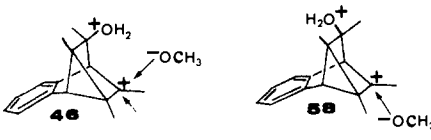
Further information is given by the quench products **61** and **62**, as only these two out of eight possible isomers are found. Both **61** and **62** are formed by nucleophilic attack on C_4 and C_7, respectively (after initial reaction at C_8 to give **76**). The second (endo) attack (at C_7 of **76**) complements that observed for **40**, which leads selectively to the exo product because of the directing effect of the OH_2^+ group. This behavior is analogous to that of **46** and **58**. Primary attack of methoxide on C_4 is unlikely. If this were the case, quench products from a second attack on both C_6 and C_7 would be expected.[42] The third possibility, attack on the "surface" of the bishomocyclopropenium unit, can be ruled out on the basis of the product stereochemistry and indicates an intact bishomo unit in **60**. Both the NMR data and the quench products suggest that the two separate charged moieties in the dication only communicate via the Colombic repulsion. This means that the longicyclic interaction, if it exists, is not sufficient to overcome this electrostatic destabilization.

Scheme III: Rationalization of the Rearrangement Path of the Dication **60**









Rearrangement to [3.3.0] Dications. Although dication **60** is comprised of two separate cation units, it exhibits extremely high selectivity in its rearrangement behavior. Remarkably, **60** isomerizes under mild conditions exclusively to **49**, but **50** forms as well at higher temperatures. A reaction path (Scheme III) that explains both products begins with formation of the dication **77**, which then undergoes "bridge flipping" to give **78** and further rearrangement to the benzo[3.2.1] dication **79**. A precedent for this transformation has been reported by Hart and Kuzuya for

(40) Hogeveen, H.; Kruchten, E. M. G. A. v. *J. Org. Chem.* **1977**, *42*, 1472.
(41) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *Angew. Chem.* **1983**, *95*, 726.
(42) Hogeveen, H.; Kruchten, E. M. G. A. v. *Top. Curr. Chem.* **1979**, *80*, 89.
(43) Kuzuya, M.; Hart, H. *Tetrahedron Lett.* **1973**, *40*, 3887, 3891; *J. Am. Chem. Soc.* **1975**, *97*, 2459; **1976**, *98*, 1551.
(44) Schwetlick, K. *Organikum*; Deutscher Verlag der Wissenschaften: Berlin, 1976.
(45) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; Ferdinand Enke Verlag: Stuttgart, 1975; Vol. 1, p 191.
(46) Siehl, H.-U., private communication.
(47) Rees, C. W.; Atkin, R., unpublished results, cited in: Horspool, W. M.; *Q. Rev., Chem. Soc.* **1969**, *23*, 204.
(48) (a) Smith, L. I.; Dobrovolny, F. I. *J. Am. Chem. Soc.* **1926**, *48*, 1420. (b) Smith, L. I.; Hac, L. R. *J. Am. Chem. Soc.* **1934**, *56*, 477.
(49) Thummel, R. P.; Cravey, W. E.; Cantu, D. B. *J. Org. Chem.* **1980**, *45*, 1633.
(50) Teuber, H. J.; Weberli, P. A.; Pigott, F.; Brossi, A. *Org. Synth.* **1972**, *52*, 88.
(51) Ulrich, H.; Richter, R. *Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, 1977; Vol. VII/3a, p 29.
(52) Prakash, G. K. S.; Farnia, M.; Keyanian, S., Olah, G. A.; Kuhn, H. J.; Schaffner, K. *J. Am. Chem. Soc.* **1987**, *109*, 911.

the bicyclo[3.2.1]octadienyl monocation.[43] The further rearrangement steps are analogous to those of the diketone system (cf. dications **38** and **39**). The only intermediate that explains the preference for **49** over **50** is, as in the case of the diketone **23**, the [4.2.0] system (**81**, **82**), whose substitution pattern influences the ring opening to the eight-membered ring.

Conclusions

All our results suggest that bicyclic longicyclic interactions do not lead to significant stabilization. None of the reactions of the benzobarrelene diols **21** and **22**, the benzobarrelene diones **19** and **20**, and the benzobarrelenes **72** and **73** under superacid conditions at temperatures as low as −130 °C give derivatives of the barrelene dication **4**. In accord with our MNDO calculations, only in special cases can rearranged systems with the bicyclo[3.2.1] skeleton be observed. Depending on the bridgehead substituents, these dications possess different kinetic stabilities that may be attributed to the thermally forbidden ring opening in the [4.2.0] system. Bicyclo[3.3.0] dications, which are also the end products of attempts to prepare cyclooctatetraene dications,[10] are found as the thermodynamically most stable ultimate rearrangement products. The stability order for the dication systems, [2.2.2] < [4.2.0] < [3.2.1] < COT < [3.3.0], means the longicyclic interactions are less effective than Hückel aromaticity. This, in turn, is less favorable than the pericyclic "antiaromatic" bicyclo[3.3.0]octadiene system.

Experimental Section

General Procedures. Boiling points and melting points are uncorrected. Infrared spectra were recorded on Beckman spectrometers; absorptions are reported in reciprocal centimeters. Standard ^{1}H NMR were recorded on JEOL JNM-C-60-H, JEOL PMX-60, JEOL JNM-PS-100, and JEOL JNM-GX-400 spectrometers, and chemical shifts (δ) are reported downfield from internal tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; mc, multicenter), coupling constant (hertz), integration, and assignment. Standard ^{13}C NMR were recorded on JEOL JNM-PS-100 and JEOL JNM-GX-400 spectrometers and are reported (chemical shift (δ), multiplicity in the off-resonance spectrum, assignment) downfield from tetramethylsilane. Low-temperature ^{1}H and ^{13}C NMR were recorded on a JEOL JNM-PS-100 spectrometer equipped with a JNM-VT-3C temperature controller by cooling with nitrogen gas evaporated from liquid nitrogen. Mass spectra were recorded on a Varian MAT CH 4 and a Varian MAT 311 A. Elemental analyses were determined with a Heraeus CHN-RAPID. Preparative HPLC was performed on a preparative chromatograph, Du Pont 830, equipped with an UV detector and a KNAUER differential refractometer, using a 25 cm × 2.2 cm stainless steel column packed with Chrompack Lichrosorb Si-60-7. All solvents for chromatography were purified by standard procedures.[44] THF and ether were distilled from sodium–potassium alloy. SO_2ClF was prepared by a literature method[45] and twice distilled from SbF_5. Low-temperature baths used ethanol/liquid nitrogen (−120 °C) and methanol–ethanol (1:1, v/v)/liquid nitrogen (−145 °C).

Cation Generation. Standard Procedure A. To 0.4 mL of a solution of MA (SbF_5/FSO_3H, 1:1) and SO_2ClF (1:10–1:3, v/v), mixed at 0 °C in the NMR tube and cooled to −130 °C, was added under nitrogen 0.01–0.05 mmol of the precursor. The mixture was left at low temperature for some minutes after addition and then mixed vigorously to clear the solution.

Cation Generation. Standard Procedure B. The reaction was performed in a modified Siehl apparatus[46] in which vigorous mixing at temperatures down to −145 °C was possible during addition of precooled (temperature of liquid N_2) starting material. After completion of the addition (up to 2 h), the clear solution was warmed to −120 °C and transferred under nitrogen pressure into a ^{13}C NMR tube held at −150 °C.

Cation Quench Reaction. Standard Procedure C. To a mixture of 50 g of K_2CO_3 and 100 g of ice was added the ^{13}C NMR sample (directly after measurement) via a precooled glass pipet, making sure that every drop of the colored cation solution was decolorized before addition of the next drop. The mixture was treated with ether (4 × 200 mL). The combined organic layers were extracted with water (neutral) and dried over $MgSO_4$ (ketones) or K_2CO_3 (alcohols and methyl ethers). The solvent was removed under aspirator vacuum and the residue crystallized or separated by HPLC.

Cation Quench Reaction. Standard Procedure D. To a round-bottom flask containing 700 mL of 10% MeONa in MeOH (prepared by dilution of a 30% solution with dry MeOH) under nitrogen at −90 °C was added in portions under vigorous mixing the cation solution (direct ^{13}C NMR sample or analogously prepared mixture), waiting after every portion of the superacid solution until the color disappeared. While still at −90 °C, 300 mL of pentane was added and the temperature raised to 0 °C, and the two phases were separated. The alkaline mixture was diluted with the same volume of water and further extracted with pentane (2 × 300 mL). The combined organic layers were washed with water and dried over K_2CO_3. Evaporation of the solvent, separation with HPLC, and purification by crystallization gave the products.

Starting Materials. 1,4-Ethano-1,4-dihydro-1,2,3,4-tetramethyl-9,10-dioxonaphthalene (19).[47] A round-bottom flask fitted with two dropping funnels and a reflux condenser and containing 700 mL of dry 1,2-dichloroethane was purged with nitrogen and heated to 70 °C. A solution of 7.00 g (43 mmol) of tetramethyl-*o*-quinone[48] in 100 mL of dichloroethane and a suspension of freshly prepared benzenediazonium carboxylate[49] were added alternately (first the diazonium carboxylate) in such portions that the red color of the quinone was converted to the yellow color of the α-diketone **19** (vigorous gas evolution). The reaction was held at 70 °C for 15 min after completion of the addition and then allowed to cool to room temperature. Excess benzenediazonium carboxylate was destroyed with water. The solvent was evaporated and the residual oil crystallized from ethyl acetate to give 7.40 g (74%) of yellow needles: mp 144–146 °C (closed tube); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.79, 1.88 (2 s, 12 H), 7.42 (mc, 4 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 11.0, 14.0 (2 q, CH_3), 56.7 (s, bridgehead *C*), 122.6, 128.4 (2 d, aromatic *C*H), 136.3, 138.0 (2 s, *C*-ipso + *C*=*C*), 184.3 (s, *C*=O).

1,4-Ethano-1,4-dihydro-3,4-dimethyl-9,10-dioxonaphthalene (20). Compound **20** was prepared analogously to **19** from 9.00 g (66 mmol) of 3,4-dimethyl-*o*-quinone[50] (synthesized from 3,4-dimethylphenol and potassium nitrosodisulfonate[51]) in 12.60-g (90%) yield: mp 160–162 °C (closed tube); ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.00 (s, 6 H, *Me*), 4.30 (s, 2 H, bridgehead *H*), 7.39 (s, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 16.8 (q, CH_3), 61.2 (d, bridgehead *C*H), 125.5, 128.7 (2 d, aromatic *C*H), 133.1, 134.2 (2 s, *C*-ipso + *C*=*C*), 182.1 (s, *C*=O).

1,4-Ethano-1,4-dihydro-9,10-dihydroxy-1,2,3,4,9,10-hexamethylnaphthalene (21). To a solution of 50 mL (1.6 mmol) of methyllithium (80 mmol) in 400 mL of dry ether was added a solution of 8.60 g (35.8 mmol) of diketone **19** in 500 mL of dry ether dropwise under nitrogen atmosphere. After being stirred for 2 h, the reaction mixture was treated carefully with water, and the organic phase was washed to neutrality with water and dried with $CaCl_2$. Crystallization from a little chloroform gave 3.1 g (32%) of **21s**. Further crystallization from ether gave 1.50 g (15%) of **21a**. The residue was separated via HPLC with $CHCl_3$ 2-propanol (97:3, v/v): fraction 1, 1.10 g (11%) of **21a**; fraction 2, 1.50 g (15%) of **21s**; fraction 3, 0.90 g (9%) of **21t**.

21t (9-*anti*-10-*syn*-dihydroxy): mp 70–73 °C (pentane); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.42 (s, 1 H, anti O*H*), 0.82 (s, 3 H, anti *Me*), 1.16 (s, 3 H, syn *Me*), 1.30 (s, 1 H, syn O*H*), 1.67 (s, 6 H, bridgehead *Me*), 1.77 (s, 6 H, *Me*—C=C), 7.28 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 12.7, 14.4, 15.2 (3 q, 4 CH_3), 20.2, 20.8 (2 q, H_3CCOH), 52.1, 52.2 (2 s, bridgehead *C*), 80.2, 81.5 (2 s, *C*OH), 122.5, 122.6, 125 4, 125.9, (4 d, aromatic *C*H), 134.8, 137.1, 143.5, 143.8 (4 s, *C*-ipso + *C*=*C*); IR (KBr) 3530, 3440 (OH), 3055, 3020, 2975, 2920 cm^{-1}; MS (70 eV); *m/e* 254 (3, $M^+ - H_2O$), 239 (4), 221 (5), 211 (8), 184 (100), 169 (59). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.47; H, 8.79.

21a (9-*anti*-10-*anti*-dihydroxy): mp 203–205 °C (ether); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.20 (s, 6 H, syn *Me*), 1.68 (s, 6 H, bridgehead *Me*), 1.78 (s, 6 H, *Me*—C=C), 1.99 (s, 2 H, anti O*H*), 7.27 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 13.3, 14.4 (2 q, CH_3), 22.8 (q, H_3CCOH), 51.6 (s, bridgehead *C*), 77.4 (s, *C*OH), 122.6, 125.4 (2 d, aromatic *C*H, 135.6, 143.7 (2 s, *C*-ipso + *C*=*C*); IR (KBr) 3220 (OH), 3050, 3020, 2965, 2905, 2880, 2840 cm^{-1}; MS (70 eV); *m/e* 254 (4, $M^+ - H_2O$), 239 (2), 236 (2), 236 (2), 211 (6), 184 (100), 169 (37). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.70; H, 8.69.

21s (9-*syn*-10-*syn*-dihydroxy): mp 189–191 °C ($CHCl_3$); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.85 (s, 6 H, anti Me), 1.73 (s, 6 H, bridgehead *Me*), 1.79 (s, 6 H, *Me*—C=C), 2.54 (s, 2 H, syn O*H*), 7.21 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 13.2, 15.1 (2 q, CH_3), 22.4 (q, H_3CCOH), 51.8 (s, bridgehead *C*), 78.7 (s, *C*OH), 121.8, 125.4 (2 d, aromatic *C*H), 135.7, 144.4 (2 s, *C*-ipso + *C*=*C*): IR (KBr) 3305 (OH), 3060, 3010, 2980, 2930, 2900, 2850 cm^{-1}; MS (70 eV); *m/e* 254 (1, $M^+ - H_2O$), 239 (1), 236 (1), 211 (1), 184 (100), 169 (32). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.33; H, 8.96.

1,4-Ethano-1,4-dihydro-9,10-dihydroxy-3,4,9,10-tetramethylnaphthalene (22). Compound **22** was prepared analogously to **21**: 14.60 g of a light yellow oil was obtained from 15.00 g (70.8 mmol) of diketone **20** with 97 mL (1.6 mol) of methyllithium (155 mmol). Recrystallization from ether gave 1.20 g (7%) of **22a**; further crystallization from pentane/$CHCl_3$ gave 1.50 g (9%) of **22s**. Separation of the residue by

HPLC in $CHCl_3$/2-propanol (98:2, v/v) gave three fractions: fraction 1, 0.30 g (2%) of **22a**; fraction 2, 1.50 g (9%) of **22s**; fraction 3, 11.00 g (64%) of **22t**.

22t (9-*syn*-10-*anti*-dihydroxy): mp 117–119 °C (ether); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.97 (s, 4 H, anti *Me* + anti O*H*), 1.30 (s, 3 H, syn *Me*), 1.64 (s, 1 H, syn O*H*), 1.78 (s, 6 H, *Me*—C=C), 3.40, 3.43 (2 s, 2 H, bridgehead *H*), 7.18 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 17.3, 17.9 (2 q, C=CCH_3), 24.0, 24.4 (2 q, H_3CCOH), 61.2 (d, bridgehead *C*H), 77.9, 78.8 (2 s, *C*OH), 124.5, 124.9, 125.7, 126.1 (4 d, aromatic *C*H), 132.5, 133.1, 139.8, 141.4 (4 s, *C*-ipso + *C*=*C*); IR (KBr) 3620, 3560, 3440 (OH), 3080, 3060, 3025, 2980, 2930, 2910, 2860 cm^{-1}; MS (70 eV), *m/e* 156 (100, $M^+ - C_4H_8O_2$), 141 (39), 88 (24, $C_4H_8O_2$). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.53; H, 7.94.

22a (9-*anti*-10-*anti*-dihydroxy): mp 202–204 °C (ether); ^{1}H NMR (60 MHz, $CDCl_3$; the isomeric deuterio compound **71** only lacks the signal at 1.30 ppm) δ 1.30 (s, 6 H, syn *Me*), 1.78 (s, 6 H, *Me*—C=C), 2.28 (s, 2 H, anti O*H*), 3.42 (s, 2 H, bridgehead *H*), 7.19 (mc, 4 H, aromatic *H*); ^{13}C NMr (25 MHz, $CDCl_3$) δ 17.1 (q, C=CCH_3), 25.9 (q, H_3CCOH), 61.1 (d, bridgehead *C*), 125.0, 125.6 (2 d, aromatic *C*H), 133.0, 140.4 (2 s, *C*-ipso + *C*=*C*); IR (KBr) 3500, 3400 (OH), 3080, 3060, 3030, 3005, 2980, 2940, 2920, 2860 cm^{-1}; MS (70 eV), *m/e* 156 (99, $M^+ - C_4H_8O_2$), 141 (85), 88 (100, $C_4H_8O_2$). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.39; H, 8.52.

22s (9-*syn*-10-*syn*-dihydroxy): mp 187–189 °C ($CHCl_3$/pentane); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.97 (s, 6 H, anti *Me*), 1.85 (s, 6 H, *Me*—C=C), 2.75 (s, 2 H, syn O*H*), 3.47 (s, 2 H, bridgehead *H*), 7.13 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 17.9 (q, H_3CC=C), 26.1 (q, H_3CCOH), 61.0 (d, bridgehead *C*), 75.8 (s, *C*OH), 124.0, 125.6 (2 d, aromatic *C*H), 132.4, 141.3 (2 s, *C*-ipso + *C*=*C*); IR (KBr) 3400 (OH), 3040, 3020, 2990, 2930, 2920, 2900, 2870 cm^{-1}; MS (70 eV), *m/e* 156 (63, $M^+ - C_4H_8O_2$), 141 (52), 88 (100, $C_4H_8O_2$). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.53; H, 7.94.

Quench Reactions. 3,4-Dimethyl-2,10-dioxobenzobicyclo[3.2.1]octa-3,5a-diene (25). A ^{13}C NMR sample prepared from 400 mg (1.9 mmol) of diketone **20**, 3.05 g (9.6 mmol) of MA, and 2 mL of SO_2ClF (procedure A) was quenched after measurement following procedure C. Crystallization of the colorless oil gave 320 mg (80%) of **25**: mp 150–151 °C (ethyl acetate); ^{1}H NMR (60 MHz, $CDCl_3$) Chart II; ^{13}C NMR (25 MHz, $CDCl_3$) Chart II; IR (KBr) 3060, 3010, 2985, 2965, 2915, 1770, 1650 cm^{-1}; MS (70 eV); *m/e* 212 (100, M^+), 184 (15), 169 (10), 156 (88), 141 (81). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.23; H, 5.70. Found: C, 79.34; H, 5.92.

1,3,4,5-Tetramethyl-2,10-dioxobenzobicyclo[3.3.0]octa-3,5a-diene (27). Reaction of 400 mg (1.7 mmol) of diketone **19** and 2.11 g (6.7 mmol) of MA in 3 mL of SO_2ClF by procedure A and quenching of the cation solution following procedure C gave 300 mg (75%) of **27**: mp 135–138 °C (ethyl acetate); ^{1}H NMR (60 MHz, $CDCl_3$) see Chart II; ^{13}C NMR (25 MHz, $CDCl_3$) see Chart II; IR (KBr) 3060, 2980, 2940, 1760, 1660 cm^{-1}; MS (70 eV), *m/e* 240 (100, M^+), 225 (54), 212 (6), 197 (36), 184 (18), 169 (40). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.69; H, 6.49.

8-*endo*-Hydroxy-6-*endo*-methoxy-1,2,5,6,7,8-hexamethyl-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (41). Cation **40** was prepared from 500 mg (1.8 mmol) of **21t** and 3.78 g (11.9 mmol) of MA in 6 mL of SO_2ClF (procedure B) and worked up at −70 °C following procedure D. HPLC of the resulted oil with ether/light petroleum ether (9:1, v/v) gave 235 mg (45%) of **41**: mp 77.5–79.5 °C (pentane); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.66 (d, 3 H, $J \sim 1$ Hz, exo *Me*COH), 0.84 (s, 3 H, exo *Me*COMe), 1.12, 1.19, 1.33 (3 s, 9 H, cyclopropyl *Me*), 1.39 (s, 3 H, bridgehead *Me*), 3.41 (s, 3 H, endo O*Me*), 3.87 (q, 1 H, $J \sim 1$ Hz, endo O*H*), 7.00–7.35 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 6.8, 7.0, 8.9, 12.6, 17.4 (6 q, CH_3), 30.9, 38.0, 38.6 (3 s, cyclopropyl *C*), 53.1 (q, OCH_3), 55.0 (s, bridgehead *C*), 82.5, 89.5 (2 s, *C*OR), 122.2, 123.4, 124.4, 126.1, (4 d, aromatic *C*H), 139.6, 140.6 (2 s, *C*-ipso); IR (KBr) 3460 (OH), 3110, 3080, 3010, 2990, 2970, 2880, 2840 cm^{-1}; MS (70 eV), *m/e* 286 (2, M^+), 268 (1), 254 (75), 239 (42), 236 (6), 224 (12), 221 (13), 211 (100). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.61; H, 9.23.

1,3,4,5-Tetramethyl-2,8-methylene-6,7-benzobicyclo[3.3.0]octa-3,6-diene and 1,2,3,5-Tetramethyl-4,8-methylene-6,7-benzobicyclo[3.3.0]octadiene (43a,b). A ^{13}C NMR sample generated via procedure A from 450 mg (1.7 mmol) of **21a** and 3.14 g (9.9 mmol) of MA in 2 mL of SO_2ClF was after measurement worked up via procedure C and gave 280 (54%) of a light yellow oil. Chromatography on 30 g of SiO_2/Ag^+ (10% $AgNO_3$ on SiO_2 packed by evaporating a CH_3CN solution of the silver salt) gave two fractions (not fully separated): F 1, 180 mg (35%) of **43a**; F 2, 60 mg (12%) of **43b**. **43a**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.20, 1.31 (2 s, 6 H, bridgehead *Me*), 1.60, 1.70 (2 q, 6 H, $J \sim 1$ Hz, *Me*—C=C—*Me*), 4.84, 5.01, 5.08, 5.63 (4 s, 4 H, C=CH_2), 7.03–7.57 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 10.6, 18.8, 21.9, 29.7 (4 q, CH_3), 58.4, 63.6 (2 s, bridgehead *C*), 99.0, 103.9 (2 t, =CH_2), 120.5, 123.4, 127.1, 128.4 (4 d, aromatic *C*H), 131.1, 138.2, 145.6, 152.3, 153.6, 161.5 (6 s, *C*=*C*). **43b**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.30 (s, 6 H, bridgehead *Me*), 1.63, 1.75 (2 q, 6 H, $J \sim 1$ Hz, *Me*—C=C—*Me*), 4.83, 4.87, 5.18, 5.50 (4 s, 4 H, C=CH_2), 7.03–7.57 (m, 4 H, aromatic *H*). **43**: IR (neat film) 3090, 3020, 2980, 2940, 2860 cm^{-1}; MS (70 eV), *m/e* 236 (M^+).

8-*endo*-Hydroxy-6-*endo*-methoxy-1,6,7,8-tetramethyl-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (47) and 8-*endo*-Hydroxy-6-*exo*-methoxy-1,6,7,8-tetramethyl-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (48). A cation solution of **46** made analogously to procedure B from 1.00 g (4.1 mmol) of **22t** and 7.0 g (22.0 mmol) of MA in 10 mL of SO_2ClF was quenched following procedure D. HPLC with light petroleum ether/ether (9:1, v/v) gave three fractions: F 1, 180 mg (19%) of unidentified product; F 2, 330 mg (30%) of **47**; F 3, 85 mg (8%) of **48**. **47**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.70 (d, 3 H, $J \sim 1$ Hz, exo-*Me*-COH), 0.75 (s, 3 H, exo *Me*-COMe), 1.23, 1.27 (2 s, 6 H, cyclopropyl *Me*), 1.63 (s, 1 H, cyclopropyl *H*), 2.90 (s, 1 H, bridgehead *H*), 3.33 (s, 3 H, endo O*Me*), 4.10 (q, 1 H, $J \sim 1$ Hz, endo O*H*), 7.00–7.24 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) 10.3, 10.5, 16.0, 19.4 (4 q, CH_3), 35.7, 37.4 (2 s, cyclopropyl *C*-Me), 36.3 (d, cyclopropyl *C*H), 50.1 (s, OCH_3), 54.5 (d, bridgehead *C*H), 80.9, 87.4 (2 s, *C*OH), 123.9, 125.1, 125.1, 126.1 (3 d, aromatic *C*H), 136.7, 137.0 (2 s, *C*-ipso); IR (KBr) 3480 (OH), 3090, 3060, 3030, 2970, 2940, 2910, 2880, 2840 cm^{-1}; MS (70 eV), *m/e* 258 (6, M^+), 240 (8), 226 (22), 211 (33), 183 (100).

48: mp 184–187 °C (ether/pentane); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.68 (d, 3 H, $J \sim 1$ Hz, exo *Me*-COH), 1.17, 1.24 (2 s, 6 H, cyclopropyl *Me*), 1.41 (q, 1 H, $J \sim 1$ Hz, endo *OH*), 1.66 (s, 3 H, endo *Me*-COMe), 1.72 (s, 1 H, cyclopropyl *H*), 2.84 (s, 3 H, exo O*Me*), 2.87 (s, 1 H, bridgehead *H*), 7.00–7.25 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 9.0, 11.5, 21.2, 23.1 (4 q, CH_3), 34.6 (d, cyclopropyl *C*H), 37.0, 37.1 (2 s, cyclopropyl *C*-Me), 50.1 (q, OCH_3), 58.4 (d, bridgehead *C*H), 80.5, 81.5 (2 s, *C*OR), 123.9, 125.1, 125.1, 126.1 (4 d, aromatic *C*H), 136.9, 137.4 (2 s, *C*-ipso); IR (KBr) 3450 (OH), 3080, 3060, 3020, 2960, 2930, 2910, 1880, 2840 cm^{-1}; MS (70 eV), *m/e* 258 (30 M^+), 240 (8), 226 (22), 211 (33), 183 (100). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.17; H, 8.65.

8-*exo*-Hydroxy-2-*exo*-methoxy-1,2,3,4,5,8-hexamethyl-6,7-benzobicyclo[3.2.1]octa-3,6-diene (55). By following procedure B the cation **54** was generated from 600 mg (2.2 mmol) of **21a**, 3.50 g (11.1 mmol) of MA, and 6 mL of SO_2ClF. Workup (procedure C) and HPLC with light petroleum ether/ether (1:1, v/v) gave after crystallization 290 mg (51%) of **55**: mp 102–105 °C (pentane); ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.16 (br s, 3 H, endo *Me*-COH), 1.22, 1.28, 1.36 (3 s, 9 H, bridgehead *Me* + endo *Me*-COMe), 1.32, 1.52 (2 q, 6 H, $J \sim 1$ Hz, *Me*—C=C—*Me*), 3.32 (s, 3 H, exo O*Me*), 5.23 (br s, 1 H, exo O*H*), 7.00–7.20 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 10.3, 11.7, 12.0, 12.4, 13.1, 20.9 (6 q, CH_3), 54.7, 56.1 (2 s, bridgehead *C*), 51.0 (q, OCH_3), 80.2, 84.4 (2 s, *C*OR), 123.6, 125.4, 127.2, 128.0 (4 d, aromatic *C*H), 131.6, 137.5, 143.5, 146.3 (4 s, *C*-ipso + *C*=*C*); IR (KBr) 3420, 3390 (OH), 3090, 3050, 3010, 2980, 2950, 2910, 2860, 2820, cm^{-1}; MS (70 eV), *m/e* 286 (1, M^+), 254 (100), 239 (52), 236 (24), 236 (24), 224 (17), 221 (56), 211 (82). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.39; 9.24.

8-*exo*-Hydroxy-6-*exo*-methoxy-1,6,7,8-tetramethyl-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (59), 6-*exo*,8-*exo*-Dimethoxy-1,6,7,8-tetramethyl-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (61), and 4-*exo*,8-*endo*-Dimethoxy-5,6,7,8-tetramethyl-2,3-benzobicyclo[3.2.1]octa-2,6-diene (62). After generation of cation **58** at −120 °C from 860 mg (3.5 mmol) of diol **22a**, 6.70 g (21.1 mmol) of MA, and 10.7 mL of SO_2ClF, the mixture was warmed for 0.5 h to −85 °C and cooled again to −100 °C. Workup following procedure D and HPLC with ether/light petroleum ether (1:1, v/v) gave three fractions: F 1, 110 mg (11%) of **61**: F 2, 200 mg (22%) of **60**; F 3, 70 mg (8%) of **62**.

59: mp 96–98 °C (pentene); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.79 (q, 1 H, J = 1 Hz, exo O*H*), 1.20 (s, 6 H, cyclopropyl *Me*), 1.45 (d, 3 H, $J \sim 1$ Hz, endo *Me*-COH), 1.51 (s, 3 H, endo Me-COMe), 1.79 (s, 1 H, cyclopropyl *H*), 2.83 (s, 3 H, exo O*Me*), 3.13 (s 1 H, bridgehead *H*), 7.03–7.40 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 10.7, 11.1, 21.6, 23.9 (4 q, CH_3), 36.3 (d, cyclopropyl *C*H), 37.5, 38.0 (bridgehead *C*-Me), 50.0 (q, OCH_3), 59.0 (d, bridgehead *C*H), 82.5, 89.5 (2 s, *C*OR), 122.2, 123.4, 124.4, 126.1 (4 d, aromatic *C*H), 139.6, 140.6 (2 s, *C*-ipso); IR (KBr) 3580 (OH), 3090, 3060, 3030, 3005, 2990, 2950, 2910, 2880, 2840, 1615 cm^{-1}; MS (70 eV); *m/e* 258 (62, M^+), 240 (25), 226 (15), 225 (19), 211 (27), 209 (23), 193 (47), 183 (100). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.71; H, 8.68.

61: mp 139–141 °C (pentane); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.20 (s, 6 H, cyclopropyl *Me*), 1.50 (s, 6 H, endo *Me*-COMe), 1.85 (s, 1 H, cyclopropyl *H*), 2.83 (s, 6 H, exo O*Me*), 3.28 (s, 1 H, bridgehead *H*),

7.01–7.38 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) 11.2, 21.5 (2 q, CH_3), 36.5 (d, cyclopropyl *C*H), 36.8 (s, cyclopropyl *C*-Me), 49.8 (q, OCH_3), 55.6 (d, bridgehead *C*H), 79.5 (s, *C*OMe), 123.4, 124.5, 124.9, 125.8 (4 d, aromatic *C*H), 135.1, 138.2 (2 s, *C*-ipso); IR (KBr) 3090, 3060, 3030, 3020, 3000, 2970, 2960, 2910, 2880, 2840, 1620 cm^{-1}; MS (70 eV), *m/e* 272 (100, M$^+$), 257 (5), 240 (61), 225 (55), 208 (76), 193 (76). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.47; H, 8.87.

62: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 3 H, 5-*Me*), 1.34 (s, 3 H, 8-exo *Me*), 1.49 (q, 3 H, $J \sim 1$ Hz, 6-*Me*), 1.54 (q, 3 H, $J \sim 1$ Hz, 7-*Me*), 2.90 (s, 1 H, 1-*H*), 2.93 (s, 3 H, 8-endo O*Me*), 3.71 (s, 3 H, 4-*exo* O*Me*), 3.86 (s, 1 H, 4-endo *H*), 6.95, 7.06, 7.18, 7.38 (4 mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 9.0, 12.6, 13.2, 17.1 (4 q, CH_3), 50.1, 56.2 (2 q, OCH_3), 58.4, 63.0 (2 d, bridgehead *C*H), 81.4, 84.4 (2 s, *C*OMe), 125.6, 125.8, 126.4, 128.4 (4 d, aromatic *C*H), 132.6, 138.9, 139.9, 142.4 (4 s, *C*-ipso + *C*=*C*); IR (neat film) 3060, 3030, 3010, 2950, 2920, 2900, 2870, 2840, 2805 cm^{-1}; MS (70 eV), *m/e* 272 (2, M$^+$), 257 (1), 240 (42), 225 (35), 208 (100), 193 (62).

4-*endo*-Methoxy-2,3,5,8-tetramethyl-6,7-benzobicyclo[3.3.0]octa-2,6,8-triene (63). Reaction of 470 mg (1.9 mmol) of diol **22a**, 3.50 g (11.1 mmol) of MA, and 1.5 mL of SO_2ClF (procedure B) gave cation **58**, which was selectively rearranged to **49** (slow warming to −70 °C during the NMR measurement). Workup (procedure D) and HPLC with ether/light petroleum ether (1:1, v/v) gave 100 mg (22%) of **63**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.15 (s, 3 H, 5-*Me*), 1.95, 2.12 (2 br s, 6 H, 2-*Me*, 3-*Me*), 2.18 (s, 3 H, 8-*Me*), 3.06 (s, 3 H, endo O*Me*), 4.02 (br s, 1 H, 4-exo *H*), 7.28 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 11.0, 12.4, 14.2, 27.8 (4 q, CH_3), 56.2 (q, OCH_3), 61.6 (s, *C*-5), 89.4 (d, *C*-4), 119.6, 123.1, 123.8 126.5 (4 d, aromatic *C*H), 123.8, 131.1, 144.6, 148.0, 149.8, 160.1 (6 s, *C*-ipso + *C*=*C*); IR (neat film) 3060, 3040, 3005, 2960, 2910, 2860, 2820, 1595 cm^{-1}; MS (70 eV), *m/e* 240 (72, M$^+$), 225 (34), 210 (42), 209 (100), 208 (42), 195 (23), 195 (23), 194 (42), 193 (78).

9-*endo*-Hydroxy-1,2,5,6-*endo*,7,9-hexamethyl-8-oxa-3,4-benzo-[3.3.1.0^{2,7}]non-3-ene (66) and 9-*endo*-Hydroxy-1,2,5,6-*exo*,7,9-hexamethyl-8-oxa-3,4-benzotricyclo[3.2.1.0^{2,7}]non-3-ene (67). A ^{13}C NMR sample (prepared via procedure A) consisting of 400 mg (1.5 mmol) of **21s**, 2.33 g (7.4 mmol) of MA, and 2 mL of SO_2ClF was quenched after measurement (ratio 4:1 = **64**:**65**; highest temperature −50 °C) following procedure D. HPLC with light petroleum ether/ether (4:1, v/v) gave two isolated fractions; F 1, 200 mg (50%) of **66**; F 2, 40 mg (10%) of **67**. **66**: mp 88–90 °C (pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.42 (d; 3 H, $J \sim 1$ Hz, 9-exo *Me*), 1.11, 1.12 (2 s, 6 H, 2-*Me*, 5-*Me*), 1.12 (~q, 1 H, $J = 7$ Hz, 6-exo *H*), 1.20 (~d, 3 H, $J = 7$ Hz, 6-endo *Me*), 1.52, 1.73 (2 s, 6 H, 1-*Me*, 7-*Me*), 3.11 (q, 1 H, $J \sim 1$ Hz, endo O*H*), 7.28 (mc, 4 H, aromatic *H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1 (q, 6-CH_3), 13.0 (q, 5-CH_3), 13.3 (q, 2-CH_3), 14.5 (q, 1-CH_3), 18.3 (q, 7-CH_3), 19.2 (q, 9-CH_3), 45.3 (d, *C*-6), 45.6 (s, *C*-5), 48.1 (s, *C*-2), 75.8 (s, *C*-9), 86.5 (s, *C*-7), 86.8 (s, *C*-1), 120.5, 123.8, 125.7, 126.9 (4 d, aromatic *C*H), 134.7 (s, *C*-3), 148.9 (s, *C*-4); IR (KBr) 3500 (OH), 3060, 3030, 2980, 2950, 2930, 2860 cm^{-1}: MS (70 eV), *m/e* 272 (29, M$^+$), 257 (17), 254 (5), 239 (2), 229 (2), 211 (5), 199 (13), 200 (22), 185 (100). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.17; H, 8.90.

67: mp 56–60 °C (pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (d, 3 H, $J = 7$ Hz, 6-exo *Me*), 0.49 (s, 3 H, 9-exo *Me*), 1.09 (s, 3 H, 1-*Me*), 1.13 (s, 3 H, 7-*Me*), 1.51 (s, 3 H, 5-*Me*), 1.68 (s, 3 H, 2-*Me*), 2.16 (q, 1 H, $J = 7$ Hz, 6-endo *H*), 3.62 (br s, 1 H, endo O*H*), 7.17–7.27 (m, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) 11.2, 12.7, 13.1, 14.6 (4 q, 6-CH_3, 5-CH_3, 2-CH_3, 1-CH_3), 17.9, 18.4 (2 q, 7-CH_3, 9-CH_3), 44.2 (d, *C*-6), 47.7, 48.5 (2 s, *C*-5, *C*-2), 75.1 (s, *C*-9), 86.6, 88.1 (2 s, *C*-7, *C*-1), 123.4, 123.5, 125.6, 126.7 (4 d, aromatic *C*H), 135.4, 144.3 (2 s, *C*-3, *C*-4); IR (KBr) 3500 (OH), 3050, 3020, 2970, 2940, 2880 cm^{-1}; MS (70 eV), *m/e* 272 (29, M$^+$), 257 (29), 254 (10), 239 (2), 229 (2), 211 (2), 200 (20), 199 (12), 185 (100). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.09; H, 8.60.

Benzobarrelene. 1,4-Etheno-1,4-dihydro-1,2,3,4,9,10-hexamethylnaphthalene (72). Hexamethylbenzene (32.4 g, 0.2 mol) was dissolved in 800 mL of dry 1,2-dichloroethane and heated to 75 °C under nitrogen. Benzenediazonium carboxylate [prepared from 13.7 g (0.1 mol) of anthranilic acid and 21.0 g (23.8 mL, 0.18 mol) of amyl nitrite][49] suspended in 100 mL of dry 1,2-dichloroethane was added dropwise to the hot solution over 1 h. The brown solution was stirred a further 2 h and cooled. The solvent was evaporated, the crude product was filtered over 300 g of SiO_2 with CCl_4, and 7.0 g (22%) of starting material was recovered by recrystallization from ethanol. Chromatography with light petroleum ether on 1000 g of SiO_2 gave three fractions. Recrystallization of fraction 3 from 500 mL of ethanol gave 3.50 g (15%) of **72**. A second crystallization gave an additional 2.60 g (11%) of not fully purified product: mp 168–170 °C (ethanol); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.67 (s, 12 H, C=C—*Me*), 1.83 (s, 6 H, bridgehead *Me*), 7.03 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 13.4 (q, C=CCH_3), 14.7 (q, bridgehead CH_3), 53.2 (s, bridgehead *C*), 118.2, 122.8 (2 d, aromatic *C*H), 141.68 (s, *C*=*C*), 151.1 (s, *C*-ipso); IR (KBr) 3080, 3060, 3005, 2970, 2940, 2915, 2895, 2845 cm^{-1}; MS (70 eV), *m/e* 314 (1, M$^+$), 184 (100), 169 (19). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.95; H, 9.11.

1,4-Etheno-1,3-dihydro-2,3,9,10-tetramethylnaphthalene (73). Compound **73** was prepared analogously to **72**. Durene (26.8 g, 0.2 mol) reacted with the same amount of benzenediazonium carboxylate to give 31.5 g of a red-brown oil. Durene (21.0 g, 80%) was recovered by three recrystallizations from light petroleum ether. The fourth crystallization gave a mixture of durene, biphenylene, and product (1:1:1). Chromatography with pentene on SiO_2 gave 150 mg (2.5% relative to unrecovered starting material) of **72** as the third fraction. Recrystallization from ethanol gave 130 mg (2.2%) of colorless needles: mp 200–203 °C (ethanol); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.77 (s, 12 H, C=C-*Me*), 4.09 (s, 2 H, bridgehead *H*), 7.01 (mc, 4 H, aromatic *H*); ^{13}C NMR (25 MHz, $CDCl_3$) δ 16.4 (q, C=CCH_3, 60.7 (d, bridgehead *C*H), 120.5, 123.2 (2 d, aromatic *C*H), 138.3 (s, *C*=*C*), 147.2 (s, *C*-ipso); IR (KBr) 3060, 3000, 2960, 2945, 2905, 2895, 2840 cm^{-1}; ms (70 eV), *m/e* 210 (85, M$^+$), 195 (100), 180 (32), 165 (21), 156 (27), 141 (22). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.30; H, 8.70.

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